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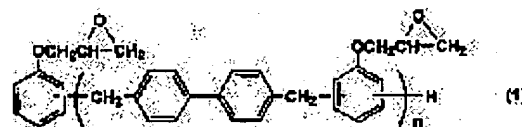
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(54) EPOXY RESIN, EPOXY RESIN COMPOSITION AND CURED PRODUCT THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an epoxy resin with excellent solubility in solvents, giving a cured product having excellent heat resistance, moistureproofness, adhesiveness and low dielectric properties.

SOLUTION: This epoxy resin is expressed by general formula (1) (where n is an average value in a range of 0.1 to 6.0) and characterized in that the softening point is 63°C or higher, and the ratio (A/B) of the integrated value (A) of a peak existing in 35 to 37 ppm to the integrated value (B) of a peak existing in 40 to 42 ppm is 1.45 or more in the ¹³C-NMR spectrum.



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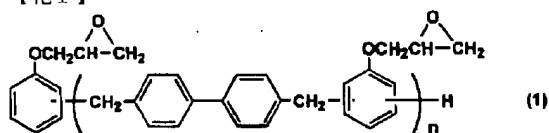
(54) 【発明の名称】 エポキシ樹脂、エポキシ樹脂組成物及びその硬化物

(57) 【要約】

【課題】 溶剤溶解性に優れ、その硬化物が、耐熱性、耐湿性、密着性、低誘電性に優れたエポキシ樹脂を提供すること。

【解決手段】 一般式 (1)

【化1】

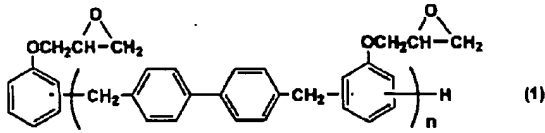


(式中、nは平均値であり、0.1～6.0を示す。)で表され、その¹³C-NMRスペクトルにおいて、35～37ppmに存在するピークの積分値(A)と40～42ppmに存在するピークの積分値(B)の比(A/B)が1.45以上、かつその軟化点が63℃以上であることを特徴とするエポキシ樹脂。

【特許請求の範囲】

【請求項1】一般式(1)

【化1】



(式中、nは平均値であり、0.1～6.0の正数を示す。)で表され、その¹³C-NMRスペクトルにおいて、35～37ppmに存在するピークの積分値(A)と40～42ppmに存在するピークの積分値(B)の比(A/B)が1.45以上、かつその軟化点が63℃以上であることを特徴とするエポキシ樹脂。

【請求項2】請求項1記載のエポキシ樹脂及び硬化剤を含有してなるエポキシ樹脂組成物。

【請求項3】硬化促進剤を含有する請求項2記載のエポキシ樹脂組成物。

【請求項4】請求項2または3記載のエポキシ樹脂組成物を硬化してなる硬化物。

【請求項5】請求項2または3記載のエポキシ樹脂組成物を溶剤に溶解してなるワニス。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は高信頼性半導体封止用を始めとする電気・電子部品絶縁材料用、及び積層板(プリント配線板)やCFRP(炭素繊維強化プラスチック)を始めとする各種複合材料用、接着剤、塗料等に有用なエポキシ樹脂、これを含むエポキシ樹脂組成物及びその硬化物に関するものである。

【0002】

【従来の技術】エポキシ樹脂は作業性及びその硬化物の優れた電気特性、耐熱性、接着性、耐湿性(耐水性)等により電気・電子部品、構造用材料、接着剤、塗料等の分野で幅広く用いられている。

【0003】近年特に電気・電子分野においてはその発展に伴い、耐熱性、耐湿性、密着性、低誘電性等の諸特性の一層の向上が求められている。また、構造材としては航空宇宙材料、レジャー・スポーツ器具用途等において軽量で機械特性の優れた材料が求められている。これらの要求に対しエポキシ樹脂について多くの提案がなされているが、ワニス状で使用する用途においては、エポキシ樹脂の溶剤に対する溶解性が悪いため、ワニスの調製前に溶剤に溶解させた状態で保管しておくことと結晶状の析出物が観察される等の問題が生ずるものがあった。

【0004】

【発明が解決しようとする課題】本発明は、その硬化物において優れた耐熱性、耐湿性(耐水性)、低誘電性を示す電気・電子部品用絶縁材料(高信頼性半導体封止材料など)及び積層板(プリント配線板など)やCFRP

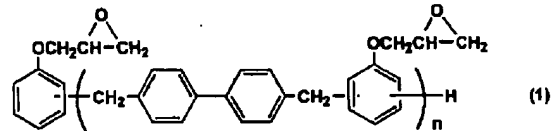
を始めとする各種複合材料用、接着剤、塗料等に有用で溶剤溶解性に優れたエポキシ樹脂、それらを含有するエポキシ樹脂組成物及びその硬化物を提供することを目的とする。

【0005】

【課題を解決するための手段】本発明者らは前記のような特性を持つエポキシ樹脂について鋭意研究の結果、本発明を完成した。即ち、本発明は、(1)一般式(1)

【0006】

【化2】



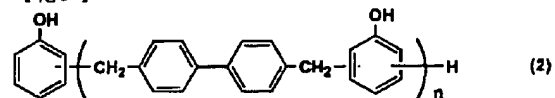
【0007】(式中、nは平均値であり、0.1～6.0の正数を示す。)で表され、その¹³C-NMRスペクトルにおいて、35～37ppmに存在するピークの積分値(A)と40～42ppmに存在するピークの積分値(B)の比(A/B)が1.45以上、かつその軟化点が63℃以上であることを特徴とするエポキシ樹脂、(2)前記(1)記載のエポキシ樹脂及び硬化剤を含有してなるエポキシ樹脂組成物、(3)硬化促進剤を含有する前記(2)記載のエポキシ樹脂組成物、(4)前記(2)または(3)記載のエポキシ樹脂組成物を硬化してなる硬化物、(5)前記(2)または(3)記載のエポキシ樹脂組成物を溶剤に溶解してなるワニスに関する。

【0008】

【発明の実施の形態】本発明のエポキシ樹脂は、式(2)

【0009】

【化3】



【0010】(式中、nは平均値であり、0.1～6.0の正数を示す。)で表されるフェノールアルルキル樹脂とエビハロヒドリンとを反応させるグリシジル化反応により得ることができる。用いる式(2)のフェノールアルルキル樹脂は、例えば特開平8-143648号に示されているように式(3)

【0011】

【化4】



【0012】(Xはアルコキシ基を示す。)で示されるビスフェニル誘導体とフェノールを反応させることにより得られる。尚、前記フェノールアルルキル樹脂を得る際

のビフェニル誘導体とフェノールの使用割合は、反応に溶媒を使用する場合、その種類によって異なる可能性があり、得られる樹脂につきA/Bが上記条件を満たすよう適宜決定され、一概には言えないが無溶媒で反応を行う場合、ビフェニル誘導体1モルに対してフェノールが通常1.1～2.9モル、好ましくは1.5～2.8モルである。

【0013】本発明のエポキシ樹脂を得る際のグリシジル化反応に使用されるエピハロヒドリンとしては、エピクロロヒドリン、エピブロムヒドリン、エピヨードヒドリン等があるが、工業的に入手し易く安価なエピクロロヒドリンが好ましい。この反応は従来公知の方法に準じて行うことが出来る。

【0014】例えば、上記フェノールアラルキル樹脂とエピハロヒドリンの混合物に水酸化ナトリウム、水酸化カリウムなどのアルカリ金属水酸化物の固体を添加し、または添加しながら20～120℃で0.5～10時間反応させる。この際アルカリ金属水酸化物は水溶液を使用してもよく、その場合は該アルカリ金属水酸化物を連続的に添加すると共に反応混合物中から減圧下、または常圧下、連続的に水及びエピクロロヒドリンを留出せしめ更に分液し水は除去しエピクロロヒドリンは反応混合物中に連続的に戻す方法でもよい。

【0015】上記の方法において、エピハロヒドリンの使用量はフェノールアラルキル樹脂の水酸基1当量に対して通常0.5～20モル、好ましくは0.7～10モルである。アルカリ金属水酸化物の使用量はフェノールアラルキル樹脂の水酸基1当量に対し通常0.5～1.5モル、好ましくは0.7～1.2モルである。また、ジメチルスルホン、ジメチルスルホキシド、ジメチルホルムアミド、1,3-ジメチル-2-イミダゾリジノン等の非プロトン溶媒を添加することにより下記に定義する加水分解性ハロゲン量の低いエポキシ樹脂が得られ、このエポキシ樹脂は電子材料封止用途に特に適する。

【0016】非プロトン性極性溶媒の使用量はエピハロヒドリンの重量に対し5～200%、好ましくは10～100%である。上記の溶媒以外にもメタノール、エタノールとのアルコール類を添加することによっても反応が進み易くなる。また、トルエン、キシレン等も使用することができる。ここで加水分解性ハロゲン量とは、例えば該エポキシ樹脂をジオキサンに入れ、数十分還流しながらKOH/エタノール溶液で滴定することにより測定することができる。

【0017】またフェノールアラルキル樹脂と過剰のエピハロヒドリンの混合物にテトラメチルアンモニウムクロライド、テトラメチルアンモニウムブロマイド、トリメチルベンジルアンモニウムクロライドなどの第四級アンモニウム塩を触媒として使用し、50～150℃で1～10時間反応させ、得られるフェノールアラルキル樹脂のハロヒドリンエーテルに水酸化ナトリウム、水酸化

カリウムなどのアルカリ金属水酸化物の固体または水溶液を加え、再び20～120℃で1～10時間反応させてハロヒドリンエーテルを閉環させて本発明のエポキシ樹脂を得ることもできる。この場合の第四級アンモニウム塩の使用量はフェノール混合物の水酸基1当量に対して通常0.001～0.2モル、好ましくは0.05～0.1モルである。アルカリ金属水酸化物の使用量はフェノールアラルキル樹脂の水酸基1当量に対して通常0.8～1.5モル、好ましくは0.9～1.1モルである。

【0018】通常これらの反応生成物は水洗後、または水洗無しに加熱減圧下、過剰のエピハロヒドリン類や溶媒等を除去した後、再びトルエン、メチルイソブチルケトン等の溶媒に溶解し、水酸化ナトリウム、水酸化カリウムなどのアルカリ金属水酸化物の水溶液を加えて再び反応を行うことにより加水分解性ハロゲン濃度の低い本発明のエポキシ樹脂を得ることができる。この場合アルカリ金属水酸化物の使用量はフェノールアラルキル樹脂の水酸基1当量に対して通常0.01～0.2モル、好ましくは0.05～0.1モルである。反応温度は通常50～120℃、反応時間は通常0.5～2時間である。

【0019】反応終了後、副生した塩をろ過、水洗などにより除去し、更に加熱減圧下、トルエン、メチルイソブチルケトン等の溶媒を留去することにより加水分解性ハロゲン濃度の低い本発明のエポキシ樹脂を得ることができる。

【0020】本発明のエポキシ樹脂の¹³C-NMRスペクトルにおいて、35～37ppmに存在するピークとは芳香環上のメチレン基の結合する位置が、2,3-エポキシプロポキシ基に対してオルソ位であることを意味する。また、40～42ppmに存在するピークとは芳香環上のメチレン基の結合する位置が、2,3-エポキシプロポキシ基に対してパラ位であることを意味する。

【0021】本発明のエポキシ樹脂は、その¹³C-NMRスペクトルにおいて、35～37ppmに存在するピークの積分値(A)と40～42ppmに存在するピークの積分値(B)の比(A/B)が1.45以上、かつその軟化点が63℃以上であることが、溶剤溶解性の面から好ましい。

【0022】以下、本発明のエポキシ樹脂組成物について説明する。本発明のエポキシ樹脂組成物において単独でまたは他のエポキシ樹脂と併用して使用することができる。併用する場合、本発明のエポキシ樹脂の全エポキシ樹脂中に占める割合は30重量%以上が好ましく、特に40重量%以上が好ましい。

【0023】本発明のエポキシ樹脂と併用されうる他のエポキシ樹脂としては、ビスフェノールA、ビスフェノールF、ビスフェノールS、フルオレンビスフェノール、テルペンジフェノール、4,4'-ビフェノール、

2, 2'-ビフェノール、3, 3', 5, 5'-テトラメチル-[1, 1'-ビフェニル]-4, 4'-ジオール、ハイドロキノ、レゾルシン、ナフタレンジオール、トリス-(4-ヒドロキシフェニル)メタン、1, 1, 2, 2-テトラキス(4-ヒドロキシフェニル)エタン、フェノール類(フェノール、アルキル置換フェノール、ナフトール、アルキル置換ナフトール、ジヒドロキシベンゼン、ジヒドロキシナフタレン等)とホルムアルデヒド、アセトアルデヒド、ベンズアルデヒド、p-ヒドロキシベンズアルデヒド、o-ヒドロキシベンズアルデヒド、p-ヒドロキシアセトフェノン、o-ヒドロキシアセトフェノン、ジシクロペンタジエン、フルフルール、4, 4'-ビス(クロロメチル)-1, 1'-ビフェニル、4, 4'-ビス(メトキシメチル)-1, 1'-ビフェニル、1, 4'-ビス(クロロメチル)ベンゼン、1, 4'-ビス(メトキシメチル)ベンゼン等との重縮合物及びこれらの変性物、テトラブロモビスフェノールA等のハロゲン化ビスフェノール類、アルコール類から誘導されるグリシジルエーテル化物、脂環式エポキシ樹脂、グリシジルアミン系エポキシ樹脂、グリシジルエステル系エポキシ樹脂等の固形または液状エポキシ樹脂が挙げられるが、これらに限定されるものではない。これらは単独で用いてもよく、2種以上を用いてもよい。

【0024】本発明のエポキシ樹脂組成物は、その好ましい実施態様においては硬化剤を含有する。硬化剤としては、例えばアミン系化合物、酸無水物系化合物、アミド系化合物、フェノール系化合物などが挙げられる。用いる硬化剤の具体例としては、ジアミノジフェニルメタン、ジエチレントリアミン、トリエチレンテトラミン、ジアミノジフェニルスルホン、イソホロンジアミン、ジシアンジアミド、リノレン酸の2量体とエチレンジアミンより合成されるポリアミド樹脂、無水フタル酸、無水トリメリット酸、無水ピロメリット酸、無水マレイン酸、テトラヒドロ無水フタル酸、メチルテトラヒドロ無水フタル酸、無水メチルナジック酸、ヘキサヒドロ無水フタル酸、メチルヘキサヒドロ無水フタル酸、ビスフェノールA、ビスフェノールF、ビスフェノールS、フルオレビスフェノール、テルペンジフェノール、4, 4'-ビフェノール、2, 2'-ビフェノール、3, 3', 5, 5'-テトラメチル-[1, 1'-ビフェニル]-4, 4'-ジオール、ハイドロキノ、レゾルシン、ナフタレンジオール、トリス-(4-ヒドロキシフェニル)メタン、1, 1, 2, 2-テトラキス(4-ヒドロキシフェニル)エタン、フェノール類(フェノール、アルキル置換フェノール、ナフトール、アルキル置換ナフトール、ジヒドロキシベンゼン、ジヒドロキシナフタレン等)とホルムアルデヒド、アセトアルデヒド、ベンズアルデヒド、p-ヒドロキシベンズアルデヒド、o-ヒドロキシベンズアルデヒド、p-ヒドロキ

シアセトフェノン、o-ヒドロキシアセトフェノン、ジシクロペンタジエン、フルフルール、4, 4'-ビス(クロロメチル)-1, 1'-ビフェニル、4, 4'-ビス(メトキシメチル)-1, 1'-ビフェニル、1, 4'-ビス(クロロメチル)ベンゼン、1, 4'-ビス(メトキシメチル)ベンゼン等との重縮合物及びこれらの変性物、テトラブロモビスフェノールA等のハロゲン化ビスフェノール類、イミダゾール、BF₃-アミン錯体、グアニジン誘導体などが挙げられるが、これらに限定されるものではない。これらは単独で用いてもよく、2種以上を用いてもよい。

【0025】本発明のエポキシ樹脂組成物において硬化剤の使用量は、エポキシ樹脂のエポキシ基1当量に対して0.5~1.5当量が好ましく、0.6~1.2当量が特に好ましい。エポキシ基1当量に対して、0.5当量に満たない場合、あるいは1.5当量を超える場合、いずれも硬化が不完全になり良好な硬化物性が得られない恐れがある。

【0026】また上記硬化剤を用いる際に硬化促進剤を併用しても差し支えない。用いる硬化促進剤としては、例えば、2-メチルイミダゾール、2-エチルイミダゾール、2-フェニルイミダゾール、2-エチル-4-メチルイミダゾール等のイミダゾール類、2-(ジメチルアミノメチル)フェノール、トリエチレンジアミン、トリエタノールアミン、1, 8-ジアザビシクロ(5, 4, 0)ウンデセン-7等の第3級アミン類、トリフェニルホスフィン、ジフェニルホスフィン、トリブチルホスフィン等の有機ホスフィン類、オクチル酸スズなどの金属化合物、テトラフェニルホスホニウム・テトラフェニルボレート、テトラフェニルホスホニウム・エチルトリフェニルボレート等のテトラ置換ホスホニウム・テトラ置換ボレート、2-エチル-4-メチルイミダゾール・テトラフェニルボレート、N-メチルモルホリン・テトラフェニルボレート等のテトラフェニルボロン塩などが挙げられる。硬化促進剤を使用する場合の使用量はエポキシ樹脂100重量部に対して0.01~15重量部が必要に応じ用いられる。

【0027】更に、本発明のエポキシ樹脂組成物には、必要に応じて無機充填剤やシランカップリング材、離型剤、顔料等の種々の配合剤、各種熱硬化性樹脂を添加することができる。無機充填剤としては、結晶シリカ、溶融シリカ、アルミナ、ジルコン、珪酸カルシウム、炭酸カルシウム、炭化ケイ素、窒化ケイ素、窒化ホウ素、ジルコニア、フォステライト、ステアタイト、スピネル、チタニア、タルク等の粉体またはこれらを球形化したビーズ等が挙げられるが、これらに限定されるものではない。これらは単独で用いてもよく、2種以上を用いてもよい。これら充填剤は、エポキシ樹脂組成物の硬化物の耐熱性、耐湿性、力学的性質などの面から、エポキシ樹脂組成物中で50~90重量%を占める割合で使用する

のが好ましい。

【0028】本発明のエポキシ樹脂組成物は、上記各成分を均一に混合することにより得られる。そして、本発明のエポキシ樹脂組成物は従来知られている方法と同様の方法で容易にその硬化物とすることができる。例えば、本発明のエポキシ樹脂と硬化剤、並びに必要により硬化促進剤及び無機充填剤、配合剤、各種熱硬化性樹脂とを必要に応じて押出機、ニーダ、ロール等を用いて均一になるまで充分に混合することにより本発明のエポキシ樹脂組成物を得て、そのエポキシ樹脂組成物を溶融注法あるいはトランスファー成型法やインジェクション成型法、圧縮成型法などによって成型し、更に80～200℃で2～10時間に加熱することにより本発明の硬化物を得ることができる。

【0029】また、本発明のエポキシ樹脂は、溶剤溶解性に優れ結晶が生じないことから、本発明のエポキシ樹脂組成物を溶剤に溶解してワニスとすることにより、積層板等の接着剤として好適に使用できる。この場合例えば本発明のエポキシ樹脂組成物をトルエン、キシレン、アセトン、メチルエチルケトン、メチルイソブチルケトン、ジメチルホルムアミド、エチレングリコールモノメチルエーテル、N-メチル-2-ピロリドン等の溶剤に溶解させ、ガラス繊維、カーボン繊維、ポリエステル繊維、ポリアミド繊維、アルミナ繊維、紙などの基材に含浸させ加熱乾燥して得たプリプレグを熱プレス成形して硬化物を得たり、γ-ブチロラクトン類、N-メチルピロリドン(NMP)、N,N-ジメチルホルムアミド(DMF)、N,N-ジメチルアセトアミド、N,N-ジメチルイミダゾリジノン等のアミド系溶剤、テトラメチレンスルホン等のスルホン類、ジエチレングリコールジメチルエーテル、ジエチレングリコールジエチルエーテル、プロピレングリコール、プロピレングリコールモノメチルエーテル、プロピレングリコールモノメチルエーテルモノアセテート、プロピレングリコールモノブチルエーテル等のエーテル系溶剤、メチルエチルケトン、メチルイソブチルケトン等のケトン系溶剤、トルエン、キシレンなどの芳香族系溶剤に溶解し下記するシートを得たりすることができる。この際の溶剤は、プレブリグ用途の場合、本発明のエポキシ樹脂組成物と該溶剤の混合物中で通常10～70重量%、好ましくは15～70重量%を占める量を用いる。また、シート用途の場合、得られたワニス中の固形分濃度は通常10～80重量%、好ましくは20～70重量%となる量の溶剤を用いる。

【0030】上記ワニスをシート状にして使用する場合、ワニスをそれ自体公知のグラビアコート法、スクリーン印刷、メタルマスク法、スピンコート法などの各種塗工方法により基材上に乾燥後の厚さが所定の厚さ、例えば5～1000μmになるように塗布後乾燥して使用するが、どの塗工法を用いるかは基材の種類、形状、大き

さ、塗膜の膜厚により適宜選択される。基材としては、例えばポリアミド、ポリアミドイミド、ポリアリレート、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエーテルエーテルケトン、ポリエーテルイミド、ポリエーテルケトン、ポリケトン、ポリエチレン、ポリプロピレン等の各種高分子及び/またはその共重合体から作られるフィルム、或いは銅箔等の金属箔であり、特に好ましくは、ポリイミドフィルム、銅箔である。剥離フィルムを使用する場合はボンディングシートとして用いられる。ボンディングシートとは離型フィルムの片面に接着剤層(ワニス)を塗布したものと別の離型剤を張り合わせたもので、フレキシブル印刷配線板とフレキシブル印刷配線板とを張り合わせる場合などの接着材料として使用される。こうして得られたシートを加熱することによりシート状の硬化物を得ることが出来る。

【0031】

【実施例】以下、本発明を実施例で更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。合成例、実施例、比較例において部は重量部を意味する。なお、エポキシ当量、軟化点、溶融粘度は以下の条件で測定した。

・エポキシ当量

JIS K-7236に準じた方法で測定し、単位はg/eqである。

・軟化点

JIS K-7234に準じた方法で測定した。

・溶融粘度

150℃におけるコーンプレート法における溶融粘度
測定器械：コーンプレート(ICI)高温粘度計(RESEACH EQUIPMENT(LONDON)LTD.製)
コーンNo.：3(測定範囲0～2.00Pa・s)
試料量：0.15±0.01g

【0032】合成例1

攪拌機、温度計、コンデンサーを備えた四つ口フラスコにフェノール382部、4,4'-ビス(メトキシメチル)-1,1'-ビフェニル485部、パラトルエンスルホン酸一水和物8部を仕込み、反応温度を125℃に保ちながら4時間反応させた。その間、生成するメタノールを反応系外に留去した。反応終了後、メチルイソブチルケトン(MIBK)1500部を加え水洗を繰り返した。ついで油層から加熱減圧下、未反応フェノール及びMIBKを留去することによりフェノールアラキル樹脂(P1)615部を得た。得られたフェノールアラキル樹脂(P1)の軟化点は92℃、溶融粘度は0.91Pa・s、水酸基当量は223g/eqであった。

【0033】合成例2

合成例1において、フェノール382部を430部に変えた以外は合成例1と同様の操作を行い、フェノールアラキル樹脂(P2)726部を得た。得られたフェノ

ールアラルキル樹脂(P2)の軟化点は85℃、溶融粘度は0.47Pa・s、水酸基当量は220g/eqであった。

【0034】合成例3

合成例1において、フェノール382部を478部に変えた以外は合成例1と同様の操作を行い、フェノールアラルキル樹脂(P3)620部を得た。得られたフェノールアラルキル樹脂(P3)の軟化点は82℃、溶融粘度は0.35Pa・s、水酸基当量は215g/eqであった。

【0035】合成例4

合成例1において、フェノール382部を506部に変えた以外は合成例1と同様の操作を行い、フェノールアラルキル樹脂(P4)632部を得た。得られたフェノールアラルキル樹脂(P4)の軟化点は79℃、溶融粘度は0.25Pa・s、水酸基当量は212g/eqであった。

【0036】合成例5

合成例1において、フェノール382部を573部に変えた以外は合成例1と同様の操作を行い、フェノールアラルキル樹脂(P5)611部を得た。得られたフェノールアラルキル樹脂(P5)の軟化点は74℃、溶融粘度は0.15Pa・s、水酸基当量は211g/eqであった。

【0037】合成例6

合成例1において、フェノール382部を611部に変えた以外は合成例1と同様の操作を行い、フェノールアラルキル樹脂(P6)615部を得た。得られたフェノールアラルキル樹脂(P6)の軟化点は71℃、溶融粘度は0.12Pa・s、水酸基当量は207g/eqであった。

【0038】合成例7

攪拌機、温度計、コンデンサーを備えた四つ口フラスコにフェノール955部を仕込み、50℃で攪拌しながら4,4'-ビス(クロロメチル)-1,1'-ビフェニル1256部、バタトルエンスルホン酸一水和物10部を加え、50℃で1.5時間、70℃で1時間、80℃で2時間反応を行った。反応終了後、MIBK2500部を加え水洗を繰り返した。ついで油層から加熱減圧下、未反応フェノール及びMIBKを留去することによりフェノールアラルキル樹脂(P7)1457部を得た。得られたフェノールアラルキル樹脂(P7)の軟化点は82℃、溶融粘度は0.40Pa・s、水酸基当量は221g/eqであった。

【0039】合成例8

合成例7において、フェノール955部を1481部に変えた以外は合成例7と同様の操作を行い、フェノールアラルキル樹脂(P8)1729部を得た。得られたフェノールアラルキル樹脂(P8)の軟化点は71℃、溶融粘度は0.12Pa・s、水酸基当量は207g/eq

であった。

【0040】実施例1

合成例1で得られた樹脂(P1)446部にエピクロルヒドリン925部、ジメチルスルホキシド185部を加えて溶解後、45℃に加熱し、フレーク状水酸化ナトリウム(純度99%)82部を90分かけて添加し、その後、さらに45℃で2時間、70℃で0.5時間反応させた。ついで水洗を繰り返し中性に戻した後、油層から加熱減圧下、過剰のエピクロルヒドリンを留去し、残留物に115部のMIBKを添加し溶解した。さらにこのMIBK溶液を70℃に加熱し30重量%の水酸化ナトリウム水溶液27部を添加し、1時間反応させた後、水洗を繰り返し中性とした。ついで油層から加熱減圧下、MIBKを留去することにより本発明のエポキシ樹脂(E1)475部を得た。得られたエポキシ樹脂(E1)の¹³C-NMRスペクトル(CDCl₃,300MHz)を図1に示す。

【0041】実施例2

実施例1において、合成例1で得られた樹脂(P1)446部を合成例2で得られた樹脂(P2)439部に変えた以外は実施例1と同様の操作を行い、本発明のエポキシ樹脂(E2)474部を得た。

【0042】実施例3

実施例1において、合成例1で得られた樹脂(P1)446部を合成例3で得られた樹脂(P3)430部に変えた以外は実施例1と同様の操作を行い、本発明のエポキシ樹脂(E3)502部を得た。

【0043】実施例4

実施例1において、合成例1で得られた樹脂(P1)446部を合成例4で得られた樹脂(P4)424部に変えた以外は実施例1と同様の操作を行い、本発明のエポキシ樹脂(E4)493部を得た。

【0044】比較例1

実施例1において、合成例1で得られた樹脂(P1)446部を合成例5で得られた樹脂(P5)425部に変えた以外は実施例1と同様の操作を行い、比較用のエポキシ樹脂(E5)492部を得た。

【0045】比較例2

実施例1において、合成例1で得られた樹脂(P1)446部を合成例6で得られた樹脂(P6)414部に変えた以外は実施例1と同様の操作を行い、比較用のエポキシ樹脂(E6)500部を得た。

【0046】比較例3

実施例1において、合成例1で得られた樹脂(P1)446部を合成例7で得られた樹脂(P7)442部に変えた以外は実施例1と同様の操作を行い、比較用のエポキシ樹脂(E7)504部を得た。

【0047】比較例4

実施例1において、合成例1で得られた樹脂(P1)446部を合成例8で得られた樹脂(P8)414部に変

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えた以外は実施例1と同様の操作を行い、比較用のエポキシ樹脂(E8)500部を得た。

【0048】以上の実施例及び比較例で得られた本発明*

表1

	実施例1	実施例2	実施例3	実施例4
エポキシ当量(g/eq)	289	291	286	278
軟化点(°C)	79	73	68	65
熔融粘度(Pa·s)	0.79	0.45	0.27	0.22
A/B	1.83	1.76	1.63	1.50

【0050】

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表2

	比較例1	比較例2	比較例3	比較例4
エポキシ当量(g/eq)	278	278	295	278
軟化点(°C)	61	58	71	58
熔融粘度(Pa·s)	0.14	0.10	0.37	0.11
A/B	1.54	1.33	1.21	0.95

【0051】試験例1~8

実施例1~4で得られたエポキシ樹脂(E1)~(E4)、比較例1~4で得られたエポキシ樹脂(E5)~(E8)について、樹脂濃度が70重量%になるように溶剤としてメチルエチルケトンに溶解させ、5°Cの環境にて保管した。試験結果を表3(実施例1~4で得られ※

※た樹脂につき左からこの順)及び表4(比較例1~4で得られた樹脂につき左からこの順)に示す。なお、判定基準を以下に示す。

○:溶解後、1週間以上経過しても結晶析出無し

×:溶解後、1週間以内に結晶析出

【0052】

表3

	試験例1	試験例2	試験例3	試験例4
エポキシ樹脂	E1	E2	E3	E4
試験結果	○	○	○	○

【0053】

表4

	試験例6	試験例7	試験例8	試験例9
エポキシ樹脂	E5	E6	E7	E8
試験結果	×	×	×	×

【0054】また、実施例1~4で得られたエポキシ樹脂(E1)~(E4)及び比較例1~4で得られたエポキシ樹脂(E5)~(E6)のA/B及び軟化点についてグラフ化したものを図2に示す。上記の試験例及び比較試験例A/Bと軟化点が特定の範囲にある本発明のエポキシ樹脂は、その範囲外にあるエポキシ樹脂に比べて良好な溶剤溶解性を示す。

【0055】実施例6

実施例2で得られたエポキシ樹脂(E2)、硬化剤としてフェノールノボラック樹脂(PN-80:日本化薬(株)製、水酸基当量105g/eq、軟化点86°C)、硬化促進剤として2-エチル-4-メチルイミダゾール(2E4MZ)、希釈剤としてメチルエチルケトン(MEK)及びメチルセロソルブ(MCS)を表5の(配合)の欄に示す重量割合で配合し、ワニスを調製した。このワニスをを用いてガラスクロス(WEA18W105F115N:日東紡績(株)製)に含浸させた後、120°Cの温風乾燥機で7分乾燥させ半硬化したプリプレグを得た。上記プリプレグ8枚と銅箔(日鉦グループ★50

★ド(株)製、JTC箔、35μm)を重ね、40kgf/cm²、温度170°Cで60分加熱加圧成形を行い、ガラスクロス積層板を作成した。作成した積層板について、以下の項目及び方法でその特性の測定を行った。測定結果を表5に示す。

・ガラス転移温度

熱機械測定装置(TMA):真空理工 TM-7000
昇温速度:2°C/min.

・銅箔剥離強度

引張試験器:東洋ボールドウィン テンシロン RTM-500

引張モード:180°剥離

クロスヘッドスピード:200mm/min.

測定温度:30°C

・吸水率

試験片:5cm×5cm

100°Cの温水中で24時間煮沸した後の重量増加量(重量%)

・誘電率

JIS 6481に準拠して測定

【0056】比較例6

エポキシ樹脂として臭素化ビスフェノールA型エポキシ樹脂(エポミックR-232:三井化学(株)製、エポキシ当量483g/eq)、硬化剤としてフェノールノボラック樹脂(PN-80:日本化薬(株)製、水酸基当量105g/eq、軟化点86℃)、硬化促進剤とし*

表5

	実施例6	比較例6
(配合)		
E2	100	
R-232		100
PN-80	36	22
2E4MZ	0.3	0.3
MEK	82	73
MCS	9	8
(硬化物性)		
ガラス転移温度(℃)	140	125
銅箔剥離強度(kN/m)	2.8	1.9
吸水率(%)	0.6	0.5
誘電率	4.6	4.8

【0058】表5より本発明の硬化物は、従来一般的に使用されるビスフェノールA型エポキシ樹脂に比べて、耐熱性、密着性、耐水性に優れ、かつ低誘電性を有する。

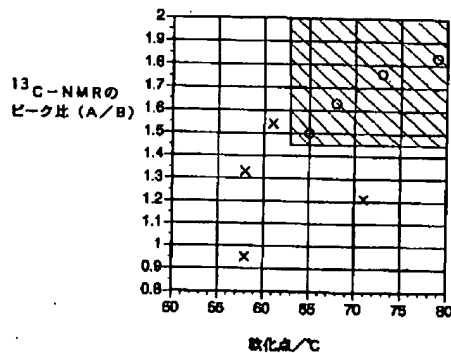
【0059】

【発明の効果】本発明のエポキシ樹脂を含有するエポキシ樹脂組成物はその硬化物において優れた耐熱性、密着性、耐湿性、低誘電性を有している。従って、電気・電子部品用絶縁材料及び積層板(プリント配線板など)やCFRPを始めとする各種複合材料、接着剤、塗料等に使用する場合に極めて有用である。

【図面の簡単な説明】

※

【図2】



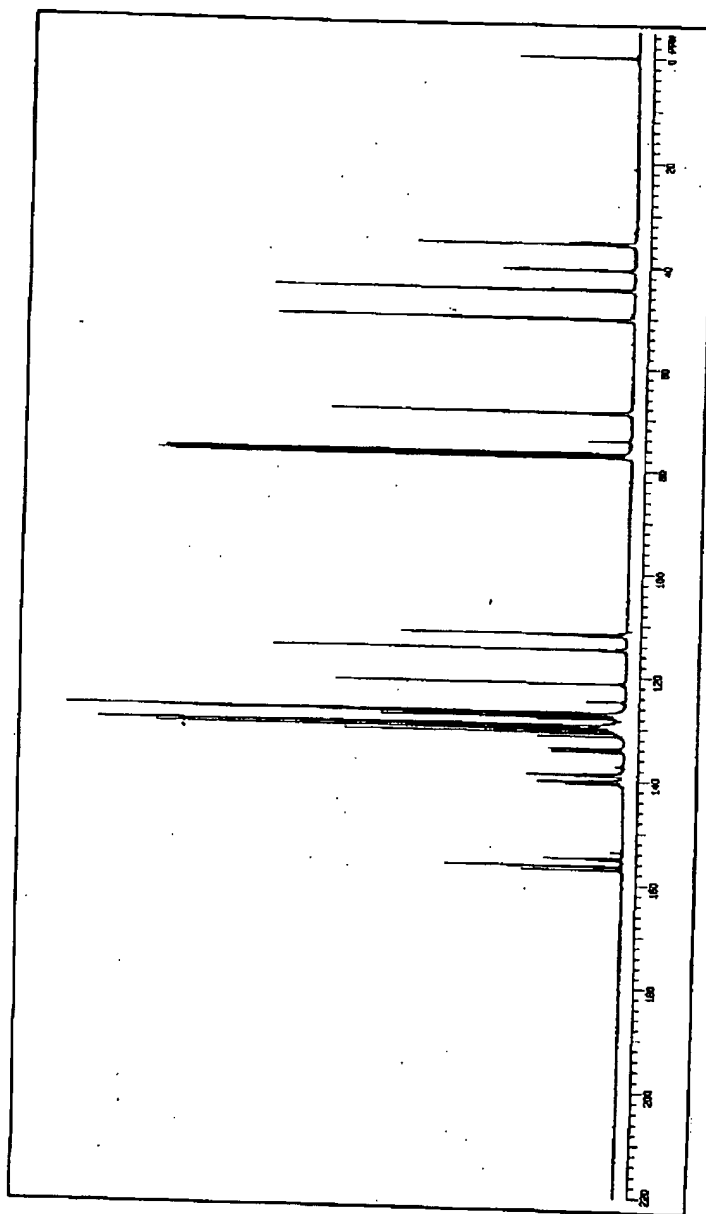
*て2-エチル-4-メチルイミダゾール(2E4MZ)、希釈剤としてメチルエチルケトン(MEK)及びメチルセロソルブ(MCS)を表5の(配合)の欄に示す重量割合で配合し、ワニスを調製した。この後の操作は実施例6と同様に行った。測定結果を表5に示す。

【0057】

※【図1】実施例1で得られた本発明のエポキシ樹脂の¹³C-NMRスペクトル。第1図において縦軸は吸収の強さを、横軸はppmをそれぞれ表す。

【図2】本発明のエポキシ樹脂及び比較用エポキシ樹脂の¹³C-NMRスペクトルにおいて35~37ppmに存在するピークの積分値(A)と40~42ppmに存在するピークの積分値(B)の比(A/B)と軟化点との関係をグラフ化した図。○は本発明のエポキシ樹脂(E1)~(E4)を、×は比較用エポキシ樹脂(E5)~(E8)をそれぞれ表す。斜線部分に本発明のエポキシ樹脂は存在している。

【図1】



* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the epoxy resin constituent which contains a useful epoxy resin and this in the various objects for composite material including the electrical and electric equipment and the objects for electronic-parts insulating materials including the object for high-reliability semi-conductor closure and a laminate (printed wired board), or CFRP (carbon fiber reinforced plastic), adhesives, a coating, etc., and its hardened material.

[0002]

[Description of the Prior Art] The epoxy resin is broadly used in the field of the electrical and electric equipment and electronic parts, a structural material, adhesives, a coating, etc. by the electrical property which was excellent in workability and its hardened material, thermal resistance, the adhesive property, moisture resistance (water resisting property), etc.

[0003] In the electrical and electric equipment and the electronic field, much more improvement in many properties, such as thermal resistance, moisture resistance, adhesion, and a low dielectric, is called for with the development especially in recent years. Moreover, as structure material, it is lightweight in an aeronautical-navigation space material, a leisure-sports instrument application, etc., and the ingredient which was excellent in the mechanical characteristic is called for. Although many proposals were made about the epoxy resin to these demands, since the solubility over the solvent of an epoxy resin was bad, when condition ***** was carried out [which was dissolved in the solvent] before preparation of a varnish, in the application used by the shape of a varnish, there were some which the problem of a crystal-like sludge being observed produces.

[0004]

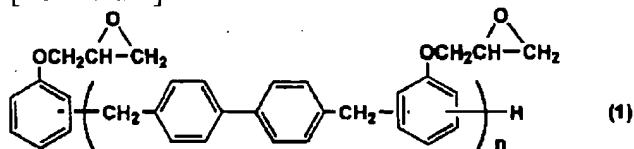
[Problem(s) to be Solved by the Invention] It is useful in the various objects for composite material including the electrical and electric equipment, the insulating materials for electronic parts (high-reliability semi-conductor closure ingredient etc.) and laminates (printed wired board etc.) in which the thermal resistance which was excellent in the hardened material, moisture resistance (water resisting property), and a low dielectric are shown, or CFRP, adhesives, coatings, etc., and this invention aims at offering the epoxy resin excellent in solvent solubility, the epoxy resin constituent containing them, and its hardened material.

[0005]

[Means for Solving the Problem] this invention persons completed this invention wholeheartedly about the epoxy resin with the above properties as a result of research. That is, this invention is (1) general formula (1).

[0006]

[Formula 2]



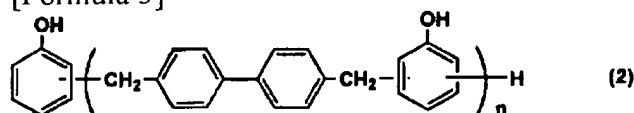
[0007] (-- among a formula, n is the average and shows the positive number of 0.1-6.0. It is expressed and sets with the ¹³C-NMR spectrum.) -- The ratio (A/B) of the integral value (A) of the peak which exists in 35-37 ppm, and the integral value (B) of the peak which exists in 40-42 ppm 1.45 or more And the epoxy resin characterized by the softening temperature being 63 degrees C or more, (2) The epoxy resin constituent which comes to contain the epoxy resin and curing agent of the aforementioned (1) publication, (3) It is related with the varnish which comes to dissolve an epoxy resin constituent the hardened material which comes to harden an epoxy resin constituent the epoxy resin constituent of the aforementioned (2) publication containing a hardening accelerator, (4) above (2), or given in (3), (5) above (2), or given in (3) in a solvent.

[0008]

[Embodiment of the Invention] The epoxy resin of this invention is a formula (2).

[0009]

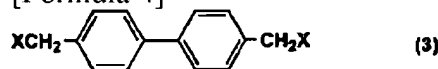
[Formula 3]



[0010] (-- among a formula, n is the average and shows the positive number of 0.1-6.0.) -- it can obtain by the glycidylized reaction to which the phenol aralkyl resin expressed and epihalohydrin are made to react. The phenol aralkyl resin of a formula (2) to be used is a formula (3) as shown in JP,8-143648,A.

[0011]

[Formula 4]



[0012] (X shows an alkoxy group.) -- it is obtained by making the biphenyl derivative and phenol which are shown react. In addition, although the operating rate of the biphenyl derivative at the time of obtaining said phenol aralkyl resin and a phenol may change with the classes, is suitably determined that A/B will fulfill the above-mentioned conditions per [which is obtained] resin and does not generally have *****, when using a solvent for a reaction, when reacting with a non-solvent, 1.1-2.9 mols of phenols are usually 1.5-2.8 mols preferably to one mol of biphenyl derivatives.

[0013] As epihalohydrin used for the glycidylized reaction at the time of obtaining the epoxy resin of this invention, although there are epichlorohydrin, EPIBUROMUHI drine compounds, EPIYODOHIDORIN, etc., cheap epichlorohydrin is [that it is easy to receive industrially] desirable. This reaction can be conventionally performed according to a well-known approach.

[0014] For example, it is made to react at 20-120 degrees C for 0.5 to 10 hours, adding the solid-state of alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, into the mixture of the above-mentioned phenol aralkyl resin and epihalohydrin, or adding into it. Under the present circumstances, while an alkali-metal hydroxide may use a water solution and adding this alkali-metal hydroxide continuously in that case, out of a reaction mixture, water and epichlorohydrin are made to distill continuously under reduced pressure or ordinary pressure, liquids may be separated further, and the approach of returning continuously during reaction mixing is [water may be removed and] sufficient as epichlorohydrin.

[0015] In the above-mentioned approach, the 0.5-20 mols of the amount of the epihalohydrin used are usually 0.7-10 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin. The 0.5-1.5 mols of the amount of the alkali-metal hydroxide used are usually 0.7-1.2 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin. Moreover, by adding nonprotic solvents, such as a dimethyl sulfone, dimethyl sulfoxide, dimethylformamide, and 1,3-dimethyl-2-imidazolidinone, an epoxy resin with the low amount of hydrolysis nature halogens defined below is obtained, and especially this epoxy resin fits an electronic ingredient closure application.

[0016] The amount of the aprotic polar solvent used is 10 - 100% preferably 5 to 200% to the weight of epihalohydrin. A reaction becomes easy to progress also by adding alcohols with a methanol and ethanol besides the above-mentioned solvent. Moreover, toluene, a xylene, etc. can be used. With the amount of hydrolysis nature halogens, for example, this epoxy resin is put into dioxane, and it can measure by titrating with KOH / ethanol solution here, flowing back for dozens minutes.

[0017] Into the mixture of phenol aralkyl resin and superfluous epihalohydrin, moreover, tetramethyl ammoniumchloride, Quarternary ammonium salt, such as a tetramethylammonium star's picture and trimethyl benzyl ammoniumchloride, is used as a catalyst. In the halohydrin ether of the phenol aralkyl resin which is made to react for 1 to 10 hours, and is obtained at 50-150 degrees C, a sodium hydroxide, The solid-state or water solutions of an alkali-metal hydroxide, such as a potassium hydroxide, are added, it can be made to be able to react at 20-120 degrees C again for 1 to 10 hours, the ring closure of the halohydrin ether can be carried out, and the epoxy resin of this invention can also be obtained. The 0.001-0.2 mols of the amount of the quarternary ammonium salt used in this case are usually 0.05-0.1 mols preferably to 1Eq of hydroxyl groups of phenol mixture. The 0.8-1.5 mols of the amount of the alkali-metal hydroxide used are usually 0.9-1.1 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin.

[0018] Usually, after rinsing or after these resultants remove scale loss pressing down, superfluous epihalohydrin, a superfluous solvent, etc. without rinsing, they can be again dissolved in solvents, such as toluene and methyl isobutyl ketone, and can obtain the epoxy resin of this invention with low hydrolysis nature halogen concentration by adding the water solution of alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, and reacting again. In this case, the 0.01-0.2 mols of the amount of the alkali-metal hydroxide used are usually 0.05-0.1 mols preferably to

1Eq of hydroxyl groups of phenol aralkyl resin. Reaction temperature is 50-120 degrees C, and reaction time is usually 0.5 - 2 hours.

[0019] Filtration, rinsing, etc. can remove the salt which carried out the byproduction after reaction termination, and the epoxy resin of this invention with low hydrolysis nature halogen concentration can be obtained by distilling off solvents, such as scale loss pressing down, toluene, and methyl isobutyl ketone, further.

[0020] In the ^{13}C -NMR spectrum of the epoxy resin of this invention, as for the peak which exists in 35-37 ppm, the location which the methylene group on a ring combines means that it is only orthochromatic to 2 and 3-epoxy propoxy group. Moreover, the peak which exists in 40-42 ppm means that the location which the methylene group on a ring combines is the para position to 2 and 3-epoxy propoxy group.

[0021] As for the epoxy resin of this invention, in the ^{13}C -NMR spectrum, it is desirable from the field of solvent solubility that the ratio (A/B) of the integral value (A) of the peak which exists in 35-37 ppm, and the integral value (B) of the peak which exists in 40-42 ppm is 1.45 or more, and the softening temperature is 63 degrees C or more.

[0022] Hereafter, the epoxy resin constituent of this invention is explained. It can be used in the epoxy resin constituent of this invention, using together with other independent or epoxy resins. When using together, the rate of occupying in all the epoxy resins of the epoxy resin of this invention has 30 desirable % of the weight or more, and especially its 40 % of the weight or more is desirable.

[0023] As other epoxy resins in which it is used together with the epoxy resin of this invention, and deals Bisphenol A, Bisphenol F, Bisphenol S, a fluorene bisphenol, - biphenol, and terpene diphenol, 4, and 4'-2, 2'-biphenol, 3, 3', 5, 5'-tetramethyl-[1 and 1'-biphenyl]-4, 4'-diol, Hydroquinone, resorcinol, naphthalene diol, tris-(4-hydroxyphenyl) methane, 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane and phenols (a phenol --) An alkylation phenol, a naphthol, an alkylation naphthol, dihydroxybenzene, Dihydroxy naphthalene, etc. formaldehyde, an acetaldehyde, A benzaldehyde, a p-hydroxy benzaldehyde, ortho hydroxybenzaldehyde, A p-hydroxy acetophenone, an o-hydroxy acetophenone, a dicyclopentadiene, A furfural, 4, the 4'-screw (chloro methyl) -1, a 1'-biphenyl, The 4 and 4'-screw (methoxymethyl) -1, - biphenyl, and 1'1, 4'-screw (chloro methyl) benzene, Polycondensation objects and these denaturation objects with 1 and 4'-screw (methoxymethyl) benzene etc., Although solids, such as a glycidyl ether ghost guided from halogenation bisphenols, such as tetrabromobisphenol A, and alcohols, cycloaliphatic epoxy resin, a glycidyl amine system epoxy resin, and a glycidyl ester system epoxy resin, or a liquefied epoxy resin is mentioned It is not limited to these. These may be used independently and may use two or more sorts.

[0024] The epoxy resin constituent of this invention contains a curing agent in the desirable embodiment. As a curing agent, an amine system compound, an acid-anhydride system compound, an amide system compound, a phenol system compound, etc. are mentioned, for example. As an example of the curing agent which can be used, diamino diphenylmethane, diethylenetriamine, Triethylenetetramine, diaminodiphenyl sulfone, isophorone diamine, A dicyandiamide, the polyamide resin compounded from the dimer and ethylenediamine of a linolenic acid, Phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, a maleic anhydride, Tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, an anhydrous methyl NAJIKKU acid, Hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, bisphenol A, Bisphenol F, Bisphenol S, a fluorene bisphenol, - biphenol, and terpene diphenol, 4, and 4'-2, 2'-biphenol, 3, 3', 5, 5'-tetramethyl-[1 and 1'-biphenyl]-4, 4'-diol, Hydroquinone, resorcinol, naphthalene diol, tris-(4-hydroxyphenyl) methane, 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane and phenols (a phenol --) An alkylation phenol, a naphthol, an alkylation naphthol, dihydroxybenzene, Dihydroxy naphthalene, etc. formaldehyde, an acetaldehyde, A benzaldehyde, a p-hydroxy benzaldehyde, ortho hydroxybenzaldehyde, A p-hydroxy acetophenone, an o-hydroxy acetophenone, a dicyclopentadiene, A furfural, 4, the 4'-screw (chloro methyl) -1, a 1'-biphenyl, The 4 and 4'-screw (methoxymethyl) -1, - biphenyl, and 1'1, 4'-screw (chloro methyl) benzene, Although halogenation bisphenols, such as polycondensation objects with 1 and 4'-screw (methoxymethyl) benzene etc. and these denaturation objects, and tetrabromobisphenol A, an imidazole, a BF_3 -amine complex, a guanidine derivative, etc. are mentioned, it is not limited to these. These may be used independently and may use two or more sorts.

[0025] In the epoxy resin constituent of this invention, the amount of the curing agent used has desirable 0.5-1.5Eq to 1Eq of epoxy groups of an epoxy resin, and especially its 0.6-1.2Eq is desirable. When not fulfilling 0.5Eq to 1Eq of epoxy groups, or when exceeding 1.5Eq, all have a possibility that hardening may become imperfection and good hardened material nature may not be obtained.

[0026] Moreover, in case the above-mentioned curing agent is used, even if it uses a hardening accelerator together, it does not interfere. As a hardening accelerator which can be used, for example 2-methylimidazole, 2-ethyl imidazole, Imidazole derivatives, such as 2-phenylimidazole and 2-ethyl-4-methylimidazole, 2-(dimethyl aminomethyl) phenol, triethylenediamine, Triethanolamine, 1, and the tertiary amine of 8-diazabicyclo (5, 4, 0) undecene-7 grade Organic phosphines, such as triphenyl phosphine, diphenylphosphine, and tributyl phosphine Metallic compounds, such as octylic acid tin, tetra-phenyl phosphonium tetraphenyl borate, Tetra-permutation phosphonium tetra-permutation borate, such as tetra-phenyl phosphonium ethyl triphenyl borate, Tetraphenylboron salts, such as 2-ethyl-4-methylimidazole tetraphenyl borate and N-methyl morpholine tetraphenyl borate, etc. are mentioned. As for the amount

of [in the case used of using a hardening accelerator], 0.01 - 15 weight section is used if needed to the epoxy resin 100 weight section.

[0027] Furthermore, to the epoxy resin constituent of this invention, various compounding agents, such as an inorganic bulking agent, silane coupling material and a release agent, and a pigment, and various thermosetting resin can be added if needed. Although the bead which conglomerated fine particles, such as a crystal silica, fused silica, an alumina, zircon, a calcium silicate, a calcium carbonate, silicon carbide, silicon nitride, boron nitride, a zirconia, a FOSUTE light, a steatite, a spinel, a titania, and talc, or these is mentioned as an inorganic bulking agent, it is not limited to these. These may be used independently and may use two or more sorts. As for these bulking agents, it is desirable to use it at a rate of occupying 50 - 90 % of the weight in an epoxy resin constituent, from fields, such as the thermal resistance of the hardened material of an epoxy resin constituent, moisture resistance, and a mechanical property.

[0028] The epoxy resin constituent of this invention is obtained by mixing each above-mentioned component to homogeneity. And the epoxy resin constituent of this invention can be easily used as the hardened material by the approach learned conventionally and the same approach. In the epoxy resin of this invention, a curing agent, and a list, as occasion demands For example, a hardening accelerator and an inorganic bulking agent, The epoxy resin constituent of this invention is obtained from fully mixing a compounding agent and various thermosetting resin until it becomes homogeneity using an extruder, a kneader, a roll, etc. if needed. The epoxy resin constituent can be cast by the melting casting method or the transfer molding method, the injection casting method, the compression casting method, etc., and the hardened material of this invention can be obtained by heating at further 80-200 degrees C in 2 - 10 hours.

[0029] Moreover, since it excels in solvent solubility and a crystal does not arise, the epoxy resin of this invention can be suitably used as adhesives, such as a laminate, by dissolving the epoxy resin constituent of this invention in a solvent, and considering as a varnish. In this case, the epoxy resin constituent of this invention Toluene, a xylene, An acetone, a methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, It is made to dissolve in solvents, such as ethylene glycol monomethyl ether and a N-methyl-2-pyrrolidone. A glass fiber, carbon fiber, polyester fiber, a polyamide fiber, an alumina fiber, Heat press forming of the prepreg which carried out stoving and which was made to carry out impregnation to base materials, such as paper, and was obtained is carried out. A hardened material OK Gamma-butyrolactone, N-methyl pyrrolidone (NMP), N,N-dimethylformamide (DMF), Amide series solvents, such as N,N-dimethylacetamide, N, and N-dimethyl imidazolidinone, Sulfones, such as tetramethylene sulfone, diethylene-glycol wood ether, Diethylene-glycol diethylether, propylene glycol, propylene glycol monomethyl ether, Ethers solvents, such as propylene-glycol-monomethyl-ether mono-acetate and the propylene glycol monobutyl ether, It can dissolve in aromatic solvents, such as ketones, such as a methyl ethyl ketone and methyl isobutyl ketone, toluene, and a xylene, and the sheet which carries out the following can be obtained. In the case of a prepreg application, the amount which occupies 15 - 70 % of the weight preferably is usually used for the solvent in this case ten to 70% of the weight in the epoxy resin constituent of this invention, and the mixture of this solvent. Moreover, in the case of a sheet application, the solid content concentration in the obtained varnish usually uses the solvent of the amount which becomes 20 - 70 % of the weight preferably ten to 80% of the weight.

[0030] Although a varnish is used drying after spreading so that the thickness after drying on a base material may turn into predetermined thickness , for example , 5-100 micrometers , in itself by the various coating approaches , such as the well-known gravure coat method , screen-stencil , the metal mask method , and a spin coat method , when using it by making the above-mentioned varnish into the shape of a sheet , it is suitably chosen by the thickness of the class of base material , a configuration , magnitude , and a paint film which coating method is used . As a base material, it is metallic foils, such as a film made, for example from various macromolecules, such as a polyamide, polyamidoimide, polyarylate, polyethylene terephthalate, polybutylene terephthalate, a polyether ether ketone, polyether imide, a polyether ketone, the poly ketone, polyethylene, and polypropylene, and/or the copolymer of those, or copper foil, and they are a polyimide film and copper foil especially preferably. When using an exfoliation film, it is used as a bonding sheet. It is used as charges of a binder in the case of having made the release agent with a bonding sheet different from what applied the adhesives layer (varnish) to one side of a mold releasing film rival, and making a flexible printed circuit plate and a flexible printed circuit plate rival etc. In this way, a sheet-like hardened material can be obtained by heating the obtained sheet.

[0031]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples. In a synthetic example, an example, and the example of a comparison, the section means the weight section. In addition, weight per epoxy equivalent, softening temperature, and melt viscosity were measured on condition that the following.

- Weight-per-epoxy-equivalent JIS Measuring by the approach according to K-7236, a unit is g/eq.
- Softening temperature JIS It measured by the approach according to K-7234.
- The melt viscosity measurement appliance in the cone plate method in 150 degrees C of melt viscosity : cone plate (ICI) elevated-temperature viscometer (product made from RESEACH EQUIPMENT(LONDON) LTD.)

Cone No.: Three (measuring range 0 - 2.00 Pa-s)

The amount of samples: 0.15**0.01g [0032] The phenol 382 section, 4, the 4'-screw (methoxymethyl) -1, the 1'-biphenyl 485 section, and the Para toluenesulfonic acid monohydrate 8 section are taught to the 4 opening flask equipped with synthetic example 1 agitator, the thermometer, and the capacitor, and it was made to react for 4 hours, keeping reaction temperature at 125 degrees C. In the meantime, the methanol to generate was distilled off out of the system of reaction. After reaction termination, the methyl-isobutyl-ketone (MIBK) 1500 section was added, and rinsing was repeated. Subsequently, the phenol aralkyl resin (P1) 615 section was obtained by distilling scale loss pressing down, an unreacted phenol, and MIBK out of an oil reservoir. The softening temperature of the obtained phenol aralkyl resin (P1) was [0.91 Pa-s and the hydroxyl equivalent of 92 degrees C and melt viscosity] 223 g/eq.

[0033] In the example 1 of synthetic example 2 composition, except having changed the phenol 382 section into the 430 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P2) 726 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P2) was [0.47 Pa-s and the hydroxyl equivalent of 85 degrees C and melt viscosity] 220 g/eq.

[0034] In the example 1 of synthetic example 3 composition, except having changed the phenol 382 section into the 478 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P3) 620 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P3) was [0.35 Pa-s and the hydroxyl equivalent of 82 degrees C and melt viscosity] 215 g/eq.

[0035] In the example 1 of synthetic example 4 composition, except having changed the phenol 382 section into the 506 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P4) 632 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P4) was [0.25 Pa-s and the hydroxyl equivalent of 79 degrees C and melt viscosity] 212 g/eq.

[0036] In the example 1 of synthetic example 5 composition, except having changed the phenol 382 section into the 573 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P5) 611 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P5) was [0.15 Pa-s and the hydroxyl equivalent of 74 degrees C and melt viscosity] 211 g/eq.

[0037] In the example 1 of synthetic example 6 composition, except having changed the phenol 382 section into the 611 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P6) 615 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P6) was [0.12 Pa-s and the hydroxyl equivalent of 71 degrees C and melt viscosity] 207 g/eq.

[0038] The phenol 955 section was taught to the 4 opening flask equipped with synthetic example 7 agitator, the thermometer, and the capacitor, 4, the 4'-screw (chloro methyl) -1, the 1'-biphenyl 1256 section, and the Para toluenesulfonic acid monohydrate 10 section were added, stirring at 50 degrees C, it performed at 70 degrees C and 50 degrees C performed the reaction at 80 degrees C for 2 hours for 1 hour for 1.5 hours. After reaction termination, the MIBK2500 section was added and rinsing was repeated. Subsequently, the phenol aralkyl resin (P7) 1457 section was obtained by distilling scale loss pressing down, an unreacted phenol, and MIBK out of an oil reservoir. The softening temperature of the obtained phenol aralkyl resin (P7) was [0.40 Pa-s and the hydroxyl equivalent of 82 degrees C and melt viscosity] 221 g/eq.

[0039] In the example 7 of synthetic example 8 composition, except having changed the phenol 955 section into the 1481 sections, the same actuation as the synthetic example 7 was performed, and the phenol aralkyl resin (P8) 1729 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P8) was [0.12 Pa-s and the hydroxyl equivalent of 71 degrees C and melt viscosity] 207 g/eq.

[0040] The epichlorohydrin 925 section and the dimethyl sulfoxide 185 section are added to the resin (P1) 446 section obtained in the example 1 of example 1 composition, and it heats at 45 degrees C after the dissolution, and it added over 90 minutes and the flake-like sodium-hydroxide (99% of purity) 82 section was made to react at 70 degrees C by 45 more degrees C after that for 0.5 hours for 2 hours. Subsequently, after repeating rinsing and returning to neutrality, scale loss pressing down and superfluous epichlorohydrin were distilled out of the oil reservoir, and MIBK of the 115 sections was added to the residue and it dissolved in it. After having heated this MIBK solution at 70 degrees C furthermore, adding 30% of the weight of the sodium-hydroxide water-solution 27 section and making it react for 1 hour, rinsing was repeated and it considered as neutrality. Subsequently, the epoxy resin (E1) 475 section of this invention was obtained by distilling scale loss pressing down and MIBK out of an oil reservoir. 13 C-NMR spectrum (CDCL3,300MHz) of the obtained epoxy resin (E1) is shown in drawing 1.

[0041] In example 2 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P2) 439 section obtained in the synthetic example 2, the same actuation as an example 1 was performed, and the epoxy resin (E2) 474 section of this invention was obtained.

[0042] In example 3 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P3) 430 section obtained in the synthetic example 3, the same actuation as an example 1 was performed, and the epoxy resin (E3) 502 section of this invention was obtained.

[0043] In example 4 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P4) 424 section obtained in the synthetic example 4, the same actuation as an example 1 was performed, and the epoxy resin (E4) 493 section of this invention was obtained.

[0044] In example of comparison 1 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P5) 425 section obtained in the synthetic example 5, the same actuation as an example 1 was performed, and the epoxy resin (E5) 492 section for a comparison was obtained.

[0045] In example of comparison 2 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P6) 414 section obtained in the synthetic example 6, the same actuation as an example 1 was performed, and the epoxy resin (E6) 500 section for a comparison was obtained.

[0046] In example of comparison 3 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P7) 442 section obtained in the synthetic example 7, the same actuation as an example 1 was performed, and the epoxy resin (E7) 504 section for a comparison was obtained.

[0047] In example of comparison 4 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P8) 414 section obtained in the synthetic example 8, the same actuation as an example 1 was performed, and the epoxy resin (E8) 500 section for a comparison was obtained.

[0048] The physical properties of the epoxy resin of this invention obtained in the above example and example of a comparison and the epoxy resin for a comparison are shown in a table 1 and a table 2.

[0049]

table 1 An example 1 An example 2 An example 3 Example 4 weight per epoxy equivalent (g/eq) 289 291 286 278 softening temperatures (degree C) 79 73 68 65 melt viscosity (Pa-s) 0.79 0.45 0.27 0.22 A/B 1.83 1.76 1.63 1.50 [0050]

table 2 The example 1 of a comparison The example 2 of a comparison The example 3 of a comparison Example of comparison 4 weight per epoxy equivalent (g/eq) 278 278 295 278 softening temperatures (degree C) 61 58 71 58 melt viscosity (Pa-s) 0.14 0.10 0.37 0.11 A/B 1.54 1.33 1.21 0.95 [0051] About epoxy resin (E5) - (E8) obtained in the epoxy resin (E1) obtained in the one to example of trial 8 examples 1-4 - (E4) the examples 1-4 of a comparison, it was made to dissolve in a methyl ethyl ketone as a solvent so that resin concentration may become 70% of the weight, and was kept in the 5-degree C environment. A test result is shown in a table 3 (it is this order from the left per [which was obtained in the examples 1-4] resin), and a table 4 (it is this order from the left per [which was obtained in the examples 1-4 of a comparison] resin). In addition, a criterion is shown below.

O : after the dissolution, even if one week or more passes, it is a crystal deposit [0052] after crystal-deposit-less x: dissolution and within one week.

table 3 [] example 1 of a trial Example 2 of a trial Example 3 of a trial Example of trial 4 epoxy resin E1 E2 E3 E4 test result O O O O [0053]

table 4 [] example 6 of a trial Example 7 of a trial Example 8 of a trial Example of trial 9 epoxy resin E5 E6 E7 E8 test result x x x x [0054]

Moreover, what was graph-ized about the epoxy resin (E5) - (E6) A/B, and softening temperature which were obtained in epoxy resin (E1) - (E4) and the examples 1-4 of a comparison which were acquired in the examples 1-4 is shown in drawing 2. The above-mentioned example of a trial and the above-mentioned example of a comparative study As for the epoxy resin of this invention which has A/B and softening temperature in the specific range, good solvent solubility is shown compared with the epoxy resin which exists out of range.

[0055] It blended at the epoxy resin (E2) obtained in the example 6 example 2, and a weight rate which it is shown in 2-ethyl-4-methylimidazole (2E4MZ) as phenol novolak resin (PN-80: the Nippon Kayaku Co., Ltd. make, hydroxyl equivalent 105 g/eq, 86 degrees C of softening temperatures), and a hardening accelerator, and shows a methyl ethyl ketone (MEK) and methyl cellosolve (MCS) in the column of (combination) of a table 5 as a diluent as a curing agent, and the varnish was prepared. After carrying out impregnation to glass fabrics (WEA18W105F115N: Nitto Boseki Co., Ltd. make) using this varnish, the prepreg which was made to dry for 7 minutes and carried out semi-hardening with the 120-degree C warm air dryer was obtained. The eight above-mentioned prepreps and copper foil (the product made from Japanese ore GURUDO, a JTC foil, 35 micrometers) were piled up, heating pressing was performed at 40 kgf/cm² and the temperature of 170 degrees C for 60 minutes, and the glass-fabrics laminate was created. About the created laminate, the property was measured by the following items and approaches. A measurement result is shown in a table 5.

- Glass-transition-temperature thermomechanometry equipment (TMA) : vacuum science and engineering TM-7000 programming rate: 2 degrees C / min

- copper foil peel strength tension test machine: -- Oriental Baldwin Tensilon RTM-500 **** mode: -- 180-degree exfoliation crosshead speed: -- 200 mm/min

measurement temperature: -- 30 degree C and water absorption test piece: -- the weight augend (% of the weight) after boiling in warm water of 5cmx5cm100 degree C for 24 hours

- Dielectric constant JIS It is based on 6481 and is measurement [0056]. as example of comparison 6 epoxy resin -- a bromination bisphenol A mold epoxy resin (EPO MIKKU R-232:Mitsui Chemicals, Inc. make --) as 483g of weight

per epoxy equivalent, eq, and a curing agent -- phenol novolak resin (PN-80:Nippon Kayaku Co., Ltd. make --) It blended at a weight rate which it is shown in 2-ethyl-4-methylimidazole (2E4MZ) as hydroxyl equivalent 105 g/eq, 86 degrees C of softening temperatures, and a hardening accelerator, and shows a methyl ethyl ketone (MEK) and methyl cellosolve (MCS) in the column of (combination) of a table 5 as a diluent, and the varnish was prepared. Next actuation was performed like the example 6. A measurement result is shown in a table 5.

[0057]

table 5 [] example 6 Example 6 of a comparison (combination)

E2 100 R-232 100 PN-80 36 22 2E4MZ 0.3 0.3 MEK 82 73 MCS 9 8 (hardened material nature)

Glass transition temperature (degree C) 140 125 Copper foil peel strength (kN/m) 2.8 1.9 Water absorption (%) 0.6 0.5

Dielectric constant 4.6 4.8 [0058] From a table 5, compared with the bisphenol A mold epoxy resin generally used conventionally, the hardened material of this invention is excellent in thermal resistance, adhesion, and a water resisting property, and has a low dielectric.

[0059]

[Effect of the Invention] The epoxy resin constituent containing the epoxy resin of this invention has the thermal resistance which was excellent in the hardened material, adhesion, moisture resistance, and a low dielectric. Therefore, it is very useful when using it for various composite material including the electrical and electric equipment, the insulating material for electronic parts and laminates (printed wired board etc.), or CFRP, adhesives, a coating, etc.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the epoxy resin constituent which contains a useful epoxy resin and this in the various objects for composite material including the electrical and electric equipment and the objects for electronic-parts insulating materials including the object for high-reliability semi-conductor closure and a laminate (printed wired board), or CFRP (carbon fiber reinforced plastic), adhesives, a coating, etc., and its hardened material.

[0002]

[Description of the Prior Art] The epoxy resin is broadly used in the field of the electrical and electric equipment and electronic parts, a structural material, adhesives, a coating, etc. by the electrical property which was excellent in workability and its hardened material, thermal resistance, the adhesive property, moisture resistance (water resisting property), etc.

[0003] In the electrical and electric equipment and the electronic field, much more improvement in many properties, such as thermal resistance, moisture resistance, adhesion, and a low dielectric, is called for with the development especially in recent years. Moreover, as structure material, it is lightweight in an aeronautical-navigation space material, a leisure-sports instrument application, etc., and the ingredient which was excellent in the mechanical characteristic is called for. Although many proposals were made about the epoxy resin to these demands, since the solubility over the solvent of an epoxy resin was bad, when condition ***** was carried out [which was dissolved in the solvent] before preparation of a varnish, in the application used by the shape of a varnish, there were some which the problem of a crystal-like sludge being observed produces.

[0004]

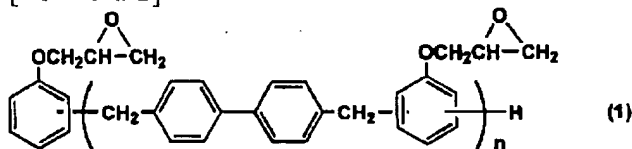
[Problem(s) to be Solved by the Invention] It is useful in the various objects for composite material including the electrical and electric equipment, the insulating materials for electronic parts (high-reliability semi-conductor closure ingredient etc.) and laminates (printed wired board etc.) in which the thermal resistance which was excellent in the hardened material, moisture resistance (water resisting property), and a low dielectric are shown, or CFRP, adhesives, coatings, etc., and this invention aims at offering the epoxy resin excellent in solvent solubility, the epoxy resin constituent containing them, and its hardened material.

[0005]

[Means for Solving the Problem] this invention persons completed this invention wholeheartedly about the epoxy resin with the above properties as a result of research. That is, this invention is (1) general formula (1).

[0006]

[Formula 2]



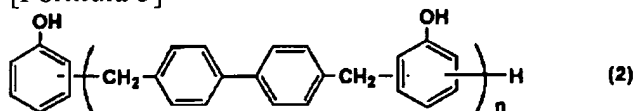
[0007] (-- among a formula, n is the average and shows the positive number of 0.1-6.0. It is expressed and sets with the ¹³C-NMR spectrum.) -- The ratio (A/B) of the integral value (A) of the peak which exists in 35-37 ppm, and the integral value (B) of the peak which exists in 40-42 ppm 1.45 or more And the epoxy resin characterized by the softening temperature being 63 degrees C or more, (2) The epoxy resin constituent which comes to contain the epoxy resin and curing agent of the aforementioned (1) publication, (3) It is related with the varnish which comes to dissolve an epoxy resin constituent the hardened material which comes to harden an epoxy resin constituent the epoxy resin constituent of the aforementioned (2) publication containing a hardening accelerator, (4) above (2), or given in (3), (5) above (2), or given in (3) in a solvent.

[0008]

[Embodiment of the Invention] The epoxy resin of this invention is a formula (2).

[0009]

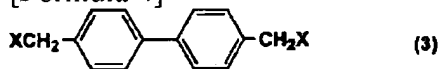
[Formula 3]



[0010] (-- among a formula, n is the average and shows the positive number of 0.1-6.0.) -- it can obtain by the glycidyl-ized reaction to which the phenol aralkyl resin expressed and epihalohydrin are made to react. The phenol aralkyl resin of a formula (2) to be used is a formula (3) as shown in JP,8-143648,A.

[0011]

[Formula 4]



[0012] (X shows an alkoxy group.) -- it is obtained by making the biphenyl derivative and phenol which are shown react. In addition, although the operating rate of the biphenyl derivative at the time of obtaining said phenol aralkyl resin and a phenol may change with the classes, is suitably determined that A/B will fulfill the above-mentioned conditions per [which is obtained] resin and does not generally have *****, when using a solvent for a reaction, when reacting with a non-solvent, 1.1-2.9 mols of phenols are usually 1.5-2.8 mols preferably to one mol of biphenyl derivatives.

[0013] As epihalohydrin used for the glycidyl-ized reaction at the time of obtaining the epoxy resin of this invention, although there are epichlorohydrin, EPIBUROMUHI drine compounds, EPIYODOHIDORIN, etc., cheap epichlorohydrin is [that it is easy to receive industrially] desirable. This reaction can be conventionally performed according to a well-known approach.

[0014] For example, it is made to react at 20-120 degrees C for 0.5 to 10 hours, adding the solid-state of alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, into the mixture of the above-mentioned phenol aralkyl resin and epihalohydrin, or adding into it. Under the present circumstances, while an alkali-metal hydroxide may use a water solution and adding this alkali-metal hydroxide continuously in that case, out of a reaction mixture, water and epichlorohydrin are made to distill continuously under reduced pressure or ordinary pressure, liquids may be separated further, and the approach of returning continuously during reaction mixing is [water may be removed and] sufficient as epichlorohydrin.

[0015] In the above-mentioned approach, the 0.5-20 mols of the amount of the epihalohydrin used are usually 0.7-10 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin. The 0.5-1.5 mols of the amount of the alkali-metal hydroxide used are usually 0.7-1.2 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin. Moreover, by adding nonprotic solvents, such as a dimethyl sulfone, dimethyl sulfoxide, dimethylformamide, and 1,3-dimethyl-2-imidazolidinone, an epoxy resin with the low amount of hydrolysis nature halogens defined below is obtained, and especially this epoxy resin fits an electronic ingredient closure application.

[0016] The amount of the aprotic polar solvent used is 10 - 100% preferably 5 to 200% to the weight of epihalohydrin. A reaction becomes easy to progress also by adding alcohols with a methanol and ethanol besides the above-mentioned solvent. Moreover, toluene, a xylene, etc. can be used. With the amount of hydrolysis nature halogens, for example, this epoxy resin is put into dioxane, and it can measure by titrating with KOH / ethanol solution here, flowing back for dozens minutes.

[0017] Into the mixture of phenol aralkyl resin and superfluous epihalohydrin, moreover, tetramethyl ammoniumchloride, Quarternary ammonium salt, such as a tetramethylammonium star's picture and trimethyl benzyl ammoniumchloride, is used as a catalyst. In the halohydrin ether of the phenol aralkyl resin which is made to react for 1 to 10 hours, and is obtained at 50-150 degrees C, a sodium hydroxide, The solid-state or water solutions of an alkali-metal hydroxide, such as a potassium hydroxide, are added, it can be made to be able to react at 20-120 degrees C again for 1 to 10 hours, the ring closure of the halohydrin ether can be carried out, and the epoxy resin of this invention can also be obtained. The 0.001-0.2 mols of the amount of the quarternary ammonium salt used in this case are usually 0.05-0.1 mols preferably to 1Eq of hydroxyl groups of phenol mixture. The 0.8-1.5 mols of the amount of the alkali-metal hydroxide used are usually 0.9-1.1 mols preferably to 1Eq of hydroxyl groups of phenol aralkyl resin.

[0018] Usually, after rinsing or after these resultants remove scale loss pressing down, superfluous epihalohydrin, a superfluous solvent, etc. without rinsing, they can be again dissolved in solvents, such as toluene and methyl isobutyl ketone, and can obtain the epoxy resin of this invention with low hydrolysis nature halogen concentration by adding the water solution of alkali-metal hydroxides, such as a sodium hydroxide and a potassium hydroxide, and reacting again. In this case, the 0.01-0.2 mols of the amount of the alkali-metal hydroxide used are usually 0.05-0.1 mols preferably to

1Eq of hydroxyl groups of phenol aralkyl resin. Reaction temperature is 50-120 degrees C, and reaction time is usually 0.5 - 2 hours.

[0019] Filtration, rinsing, etc. can remove the salt which carried out the byproduction after reaction termination, and the epoxy resin of this invention with low hydrolysis nature halogen concentration can be obtained by distilling off solvents, such as scale loss pressing down, toluene, and methyl isobutyl ketone, further.

[0020] In the ¹³C-NMR spectrum of the epoxy resin of this invention, as for the peak which exists in 35-37 ppm, the location which the methylene group on a ring combines means that it is only orthochromatic to 2 and 3-epoxy propoxy group. Moreover, the peak which exists in 40-42 ppm means that the location which the methylene group on a ring combines is the para position to 2 and 3-epoxy propoxy group.

[0021] As for the epoxy resin of this invention, in the ¹³C-NMR spectrum, it is desirable from the field of solvent solubility that the ratio (A/B) of the integral value (A) of the peak which exists in 35-37 ppm, and the integral value (B) of the peak which exists in 40-42 ppm is 1.45 or more, and the softening temperature is 63 degrees C or more.

[0022] Hereafter, the epoxy resin constituent of this invention is explained. It can be used in the epoxy resin constituent of this invention, using together with other independent or epoxy resins. When using together, the rate of occupying in all the epoxy resins of the epoxy resin of this invention has 30 desirable % of the weight or more, and especially its 40 % of the weight or more is desirable.

[0023] As other epoxy resins in which it is used together with the epoxy resin of this invention, and deals Bisphenol A, Bisphenol F, Bisphenol S, a fluorene bisphenol, - biphenol, and terpene diphenol, 4, and 4'2, 2'-biphenol, 3, 3', 5, 5'-tetramethyl-[1 and 1'-biphenyl]-4, 4'-diol, Hydroquinone, resorcinol, naphthalene diol, tris-(4-hydroxyphenyl) methane, 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane and phenols (a phenol --) An alkylation phenol, a naphthol, an alkylation naphthol, dihydroxybenzene, Dihydroxy naphthalene, etc. formaldehyde, an acetaldehyde, A benzaldehyde, a p-hydroxy benzaldehyde, ortho hydroxybenzaldehyde, A p-hydroxy acetophenone, an o-hydroxy acetophenone, a dicyclopentadiene, A furfural, 4, the 4'-screw (chloro methyl) -1, a 1'-biphenyl, The 4 and 4'-screw (methoxymethyl) -1, - biphenyl, and 1'1, 4'-screw (chloro methyl) benzene, Polycondensation objects and these denaturation objects with 1 and 4'-screw (methoxymethyl) benzene etc., Although solids, such as a glycidyl ether ghost guided from halogenation bisphenols, such as tetrabromobisphenol A, and alcohols, cycloaliphatic epoxy resin, a glycidyl amine system epoxy resin, and a glycidyl ester system epoxy resin, or a liquefied epoxy resin is mentioned It is not limited to these. These may be used independently and may use two or more sorts.

[0024] The epoxy resin constituent of this invention contains a curing agent in the desirable embodiment. As a curing agent, an amine system compound, an acid-anhydride system compound, an amide system compound, a phenol system compound, etc. are mentioned, for example. As an example of the curing agent which can be used, diamino diphenylmethane, diethylenetriamine, Triethylenetetramine, diaminodiphenyl sulfone, isophorone diamine, A dicyandiamide, the polyamide resin compounded from the dimer and ethylenediamine of a linolenic acid, Phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, a maleic anhydride, Tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, an anhydrous methyl NAJIKKU acid, Hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, bisphenol A, Bisphenol F, Bisphenol S, a fluorene bisphenol, - biphenol, and terpene diphenol, 4, and 4'2, 2'-biphenol, 3, 3', 5, 5'-tetramethyl-[1 and 1'-biphenyl]-4, 4'-diol, Hydroquinone, resorcinol, naphthalene diol, tris-(4-hydroxyphenyl) methane, 1, 1, 2, and 2-tetrakis (4-hydroxyphenyl) ethane and phenols (a phenol --) An alkylation phenol, a naphthol, an alkylation naphthol, dihydroxybenzene, Dihydroxy naphthalene, etc. formaldehyde, an acetaldehyde, A benzaldehyde, a p-hydroxy benzaldehyde, ortho hydroxybenzaldehyde, A p-hydroxy acetophenone, an o-hydroxy acetophenone, a dicyclopentadiene, A furfural, 4, the 4'-screw (chloro methyl) -1, a 1'-biphenyl, The 4 and 4'-screw (methoxymethyl) -1, - biphenyl, and 1'1, 4'-screw (chloro methyl) benzene, Although halogenation bisphenols, such as polycondensation objects with 1 and 4'-screw (methoxymethyl) benzene etc. and these denaturation objects, and tetrabromobisphenol A, an imidazole, a BF₃-amine complex, a guanidine derivative, etc. are mentioned, it is not limited to these. These may be used independently and may use two or more sorts.

[0025] In the epoxy resin constituent of this invention, the amount of the curing agent used has desirable 0.5-1.5Eq to 1Eq of epoxy groups of an epoxy resin, and especially its 0.6-1.2Eq is desirable. When not fulfilling 0.5Eq to 1Eq of epoxy groups, or when exceeding 1.5Eq, all have a possibility that hardening may become imperfection and good hardened material nature may not be obtained.

[0026] Moreover, in case the above-mentioned curing agent is used, even if it uses a hardening accelerator together, it does not interfere. As a hardening accelerator which can be used, for example 2-methylimidazole, 2-ethyl imidazole, Imidazole derivatives, such as 2-phenylimidazole and 2-ethyl-4-methylimidazole, 2-(dimethyl aminomethyl) phenol, triethylenediamine, Triethanolamine, 1, and the tertiary amine of 8-diazabicyclo (5, 4, 0) undecene-7 grade Organic phosphines, such as triphenyl phosphine, diphenylphosphine, and tributyl phosphine Metallic compounds, such as octylic acid tin, tetra-phenyl phosphonium tetraphenyl borate, Tetra-permutation phosphonium tetra-permutation borate, such as tetra-phenyl phosphonium ethyl triphenyl borate, Tetraphenylboron salts, such as 2-ethyl-4-methylimidazole tetraphenyl borate and N-methyl morpholine tetraphenyl borate, etc. are mentioned. As for the amount

of [in the case used of using a hardening accelerator], 0.01 - 15 weight section is used if needed to the epoxy resin 100 weight section.

[0027] Furthermore, to the epoxy resin constituent of this invention, various compounding agents, such as an inorganic bulking agent, silane coupling material and a release agent, and a pigment, and various thermosetting resin can be added if needed. Although the bead which conglomerated fine particles, such as a crystal silica, fused silica, an alumina, zircon, a calcium silicate, a calcium carbonate, silicon carbide, silicon nitride, boron nitride, a zirconia, a FOSUTE light, a steatite, a spinel, a titania, and talc, or these is mentioned as an inorganic bulking agent, it is not limited to these. These may be used independently and may use two or more sorts. As for these bulking agents, it is desirable to use it at a rate of occupying 50 - 90 % of the weight in an epoxy resin constituent, from fields, such as the thermal resistance of the hardened material of an epoxy resin constituent, moisture resistance, and a mechanical property.

[0028] The epoxy resin constituent of this invention is obtained by mixing each above-mentioned component to homogeneity. And the epoxy resin constituent of this invention can be easily used as the hardened material by the approach learned conventionally and the same approach. In the epoxy resin of this invention, a curing agent, and a list, as occasion demands For example, a hardening accelerator and an inorganic bulking agent, The epoxy resin constituent of this invention is obtained from fully mixing a compounding agent and various thermosetting resin until it becomes homogeneity using an extruder, a kneader, a roll, etc. if needed. The epoxy resin constituent can be cast by the melting casting method or the transfer molding method, the injection casting method, the compression casting method, etc., and the hardened material of this invention can be obtained by heating at further 80-200 degrees C in 2 - 10 hours.

[0029] Moreover, since it excels in solvent solubility and a crystal does not arise, the epoxy resin of this invention can be suitably used as adhesives, such as a laminate, by dissolving the epoxy resin constituent of this invention in a solvent, and considering as a varnish. In this case, the epoxy resin constituent of this invention Toluene, a xylene, An acetone, a methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, It is made to dissolve in solvents, such as ethylene glycol monomethyl ether and a N-methyl-2-pyrrolidone. A glass fiber, carbon fiber, polyester fiber, a polyamide fiber, an alumina fiber, Heat press forming of the prepreg which carried out stoving and which was made to carry out impregnation to base materials, such as paper, and was obtained is carried out. A hardened material OK Gamma-butyrolactone, N-methyl pyrrolidone (NMP), N,N-dimethylformamide (DMF), Amide series solvents, such as N,N-dimethylacetamide, N, and N-dimethyl imidazolidinone, Sulfones, such as tetramethylene sulfone, diethylene-glycol wood ether, Diethylene-glycol diethylether, propylene glycol, propylene glycol monomethyl ether, Ethers solvents, such as propylene-glycol-monomethyl-ether mono-acetate and the propylene glycol monobutyl ether, It can dissolve in aromatic solvents, such as ketones, such as a methyl ethyl ketone and methyl isobutyl ketone, toluene, and a xylene, and the sheet which carries out the following can be obtained. In the case of a prepreg application, the amount which occupies 15 - 70 % of the weight preferably is usually used for the solvent in this case ten to 70% of the weight in the epoxy resin constituent of this invention, and the mixture of this solvent. Moreover, in the case of a sheet application, the solid content concentration in the obtained varnish usually uses the solvent of the amount which becomes 20 - 70 % of the weight preferably ten to 80% of the weight.

[0030] Although a varnish is used drying after spreading so that the thickness after drying on a base material may turn into predetermined thickness , for example , 5-100 micrometers , in itself by the various coating approaches , such as the well-known gravure coat method , screen-stencil , the metal mask method , and a spin coat method , when using it by making the above-mentioned varnish into the shape of a sheet , it is suitably chosen by the thickness of the class of base material , a configuration , magnitude , and a paint film which coating method is used . As a base material, it is metallic foils, such as a film made, for example from various macromolecules, such as a polyamide, polyamidoimide, polyarylate, polyethylene terephthalate, polybutylene terephthalate, a polyether ether ketone, polyether imide, a polyether ketone, the poly ketone, polyethylene, and polypropylene, and/or the copolymer of those, or copper foil, and they are a polyimide film and copper foil especially preferably. When using an exfoliation film, it is used as a bonding sheet. It is used as charges of a binder in the case of having made the release agent with a bonding sheet different from what applied the adhesives layer (varnish) to one side of a mold releasing film rival, and making a flexible printed circuit plate and a flexible printed circuit plate rival etc. In this way, a sheet-like hardened material can be obtained by heating the obtained sheet.

[0031]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples. In a synthetic example, an example, and the example of a comparison, the section means the weight section. In addition, weight per epoxy equivalent, softening temperature, and melt viscosity were measured on condition that the following.

- Weight-per-epoxy-equivalent JIS Measuring by the approach according to K-7236, a unit is g/eq.
- Softening temperature JIS It measured by the approach according to K-7234.
- The melt viscosity measurement appliance in the cone plate method in 150 degrees C of melt viscosity : cone plate (ICI) elevated-temperature viscometer (product made from RESEACH EQUIPMENT(LONDON) LTD.)

• Cone No.: Three (measuring range 0 - 2.00 Pa-s)

The amount of samples: 0.15**0.01g [0032] The phenol 382 section, 4, the 4'-screw (methoxymethyl) -1, the 1'-biphenyl 485 section, and the Para toluenesulfonic acid monohydrate 8 section are taught to the 4 opening flask equipped with synthetic example 1 agitator, the thermometer, and the capacitor, and it was made to react for 4 hours, keeping reaction temperature at 125 degrees C. In the meantime, the methanol to generate was distilled off out of the system of reaction. After reaction termination, the methyl-isobutyl-ketone (MIBK) 1500 section was added, and rinsing was repeated. Subsequently, the phenol aralkyl resin (P1) 615 section was obtained by distilling scale loss pressing down, an unreacted phenol, and MIBK out of an oil reservoir. The softening temperature of the obtained phenol aralkyl resin (P1) was [0.91 Pa-s and the hydroxyl equivalent of 92 degrees C and melt viscosity] 223 g/eq.

[0033] In the example 1 of synthetic example 2 composition, except having changed the phenol 382 section into the 430 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P2) 726 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P2) was [0.47 Pa-s and the hydroxyl equivalent of 85 degrees C and melt viscosity] 220 g/eq.

[0034] In the example 1 of synthetic example 3 composition, except having changed the phenol 382 section into the 478 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P3) 620 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P3) was [0.35 Pa-s and the hydroxyl equivalent of 82 degrees C and melt viscosity] 215 g/eq.

[0035] In the example 1 of synthetic example 4 composition, except having changed the phenol 382 section into the 506 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P4) 632 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P4) was [0.25 Pa-s and the hydroxyl equivalent of 79 degrees C and melt viscosity] 212 g/eq.

[0036] In the example 1 of synthetic example 5 composition, except having changed the phenol 382 section into the 573 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P5) 611 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P5) was [0.15 Pa-s and the hydroxyl equivalent of 74 degrees C and melt viscosity] 211 g/eq.

[0037] In the example 1 of synthetic example 6 composition, except having changed the phenol 382 section into the 611 sections, the same actuation as the synthetic example 1 was performed, and the phenol aralkyl resin (P6) 615 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P6) was [0.12 Pa-s and the hydroxyl equivalent of 71 degrees C and melt viscosity] 207 g/eq.

[0038] The phenol 955 section was taught to the 4 opening flask equipped with synthetic example 7 agitator, the thermometer, and the capacitor, 4, the 4'-screw (chloro methyl) -1, the 1'-biphenyl 1256 section, and the Para toluenesulfonic acid monohydrate 10 section were added, stirring at 50 degrees C, it performed at 70 degrees C and 50 degrees C performed the reaction at 80 degrees C for 2 hours for 1 hour for 1.5 hours. After reaction termination, the MIBK2500 section was added and rinsing was repeated. Subsequently, the phenol aralkyl resin (P7) 1457 section was obtained by distilling scale loss pressing down, an unreacted phenol, and MIBK out of an oil reservoir. The softening temperature of the obtained phenol aralkyl resin (P7) was [0.40 Pa-s and the hydroxyl equivalent of 82 degrees C and melt viscosity] 221 g/eq.

[0039] In the example 7 of synthetic example 8 composition, except having changed the phenol 955 section into the 1481 sections, the same actuation as the synthetic example 7 was performed, and the phenol aralkyl resin (P8) 1729 section was obtained. The softening temperature of the obtained phenol aralkyl resin (P8) was [0.12 Pa-s and the hydroxyl equivalent of 71 degrees C and melt viscosity] 207 g/eq.

[0040] The epichlorohydrin 925 section and the dimethyl sulfoxide 185 section are added to the resin (P1) 446 section obtained in the example 1 of example 1 composition, and it heats at 45 degrees C after the dissolution, and it added over 90 minutes and the flake-like sodium-hydroxide (99% of purity) 82 section was made to react at 70 degrees C by 45 more degrees C after that for 0.5 hours for 2 hours. Subsequently, after repeating rinsing and returning to neutrality, scale loss pressing down and superfluous epichlorohydrin were distilled out of the oil reservoir, and MIBK of the 115 sections was added to the residue and it dissolved in it. After having heated this MIBK solution at 70 degrees C furthermore, adding 30% of the weight of the sodium-hydroxide water-solution 27 section and making it react for 1 hour, rinsing was repeated and it considered as neutrality. Subsequently, the epoxy resin (E1) 475 section of this invention was obtained by distilling scale loss pressing down and MIBK out of an oil reservoir. 13 C-NMR spectrum (CDCL3,300MHz) of the obtained epoxy resin (E1) is shown in drawing 1.

[0041] In example 2 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P2) 439 section obtained in the synthetic example 2, the same actuation as an example 1 was performed, and the epoxy resin (E2) 474 section of this invention was obtained.

[0042] In example 3 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P3) 430 section obtained in the synthetic example 3, the same actuation as an example 1 was performed, and the epoxy resin (E3) 502 section of this invention was obtained.

[0043] In example 4 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P4) 424 section obtained in the synthetic example 4, the same actuation as an example 1 was performed, and the epoxy resin (E4) 493 section of this invention was obtained.

[0044] In example of comparison 1 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P5) 425 section obtained in the synthetic example 5, the same actuation as an example 1 was performed, and the epoxy resin (E5) 492 section for a comparison was obtained.

[0045] In example of comparison 2 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P6) 414 section obtained in the synthetic example 6, the same actuation as an example 1 was performed, and the epoxy resin (E6) 500 section for a comparison was obtained.

[0046] In example of comparison 3 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P7) 442 section obtained in the synthetic example 7, the same actuation as an example 1 was performed, and the epoxy resin (E7) 504 section for a comparison was obtained.

[0047] In example of comparison 4 example 1, except having changed the resin (P1) 446 section obtained in the synthetic example 1 into the resin (P8) 414 section obtained in the synthetic example 8, the same actuation as an example 1 was performed, and the epoxy resin (E8) 500 section for a comparison was obtained.

[0048] The physical properties of the epoxy resin of this invention obtained in the above example and example of a comparison and the epoxy resin for a comparison are shown in a table 1 and a table 2.

[0049]

table 1 An example 1 An example 2 An example 3 Example 4 weight per epoxy equivalent (g/eq) 289 291 286 278 softening temperatures (degree C) 79 73 68 65 melt viscosity (Pa-s) 0.79 0.45 0.27 0.22 A/B 1.83 1.76 1.631.50 [0050]

table 2 The example 1 of a comparison The example 2 of a comparison The example 3 of a comparison Example of comparison 4 weight per epoxy equivalent (g/eq) 278 278 295 278 softening temperatures (degree C) 61 58 71 58 melt viscosity (Pa-s) 0.14 0.10 0.37 0.11 A/B 1.54 1.33 1.210.95 [0051] About epoxy resin (E5) - (E8) obtained in the epoxy resin (E1) obtained in the one to example of trial 8 examples 1-4 - (E4) the examples 1-4 of a comparison, it was made to dissolve in a methyl ethyl ketone as a solvent so that resin concentration may become 70% of the weight, and was kept in the 5-degree C environment. A test result is shown in a table 3 (it is this order from the left per [which was obtained in the examples 1-4] resin), and a table 4 (it is this order from the left per [which was obtained in the examples 1-4 of a comparison] resin). In addition, a criterion is shown below.

O : after the dissolution, even if one week or more passes, it is a crystal deposit [0052] after crystal-deposit-less x: dissolution and within one week.

table 3 [] example 1 of a trial Example 2 of a trial Example 3 of a trial Example of trial 4 epoxy resin E1 E2 E3 E4 test result O O O O [0053]

table 4 [] example 6 of a trial Example 7 of a trial Example 8 of a trial Example of trial 9 epoxy resin E5 E6 E7 E8 test result x x x x [0054]

Moreover, what was graph-ized about the epoxy resin (E5) - (E6) A/B, and softening temperature which were obtained in epoxy resin (E1) - (E4) and the examples 1-4 of a comparison which were acquired in the examples 1-4 is shown in drawing 2. The above-mentioned example of a trial and the above-mentioned example of a comparative study As for the epoxy resin of this invention which has A/B and softening temperature in the specific range, good solvent solubility is shown compared with the epoxy resin which exists out of range.

[0055] It blended at the epoxy resin (E2) obtained in the example 6 example 2, and a weight rate which it is shown in 2-ethyl-4-methylimidazole (2E4MZ) as phenol novolak resin (PN-80: the Nippon Kayaku Co., Ltd. make, hydroxyl equivalent 105 g/eq, 86 degrees C of softening temperatures), and a hardening accelerator, and shows a methyl ethyl ketone (MEK) and methyl cellosolve (MCS) in the column of (combination) of a table 5 as a diluent as a curing agent, and the varnish was prepared. After carrying out impregnation to glass fabrics (WEA18W105F115N: Nitto Boseki Co., Ltd. make) using this varnish, the prepreg which was made to dry for 7 minutes and carried out semi-hardening with the 120-degree C warm air dryer was obtained. The eight above-mentioned prepreps and copper foil (the product made from Japanese ore GURUDO, a JTC foil, 35 micrometers) were piled up, heating pressing was performed at 40 kgf/cm2 and the temperature of 170 degrees C for 60 minutes, and the glass-fabrics laminate was created. About the created laminate, the property was measured by the following items and approaches. A measurement result is shown in a table 5.

- Glass-transition-temperature thermomechanometry equipment (TMA) : vacuum science and engineering TM-7000 programming rate: 2 degrees C / min

- copper foil peel strength tension test machine: -- Oriental Baldwin Tensilon RTM-500 **** mode: -- 180-degree exfoliation crosshead speed: -- 200 mm/min

measurement temperature: -- 30 degree C and water absorption test piece: -- the weight augend (% of the weight) after boiling in warm water of 5cmx5cm100 degree C for 24 hours

- Dielectric constant JIS It is based on 6481 and is measurement [0056]. as example of comparison 6 epoxy resin -- a bromination bisphenol A mold epoxy resin (EPO MIKKU R-232:Mitsui Chemicals, Inc. make --) as 483g of weight

per epoxy equivalent, eq, and a curing agent -- phenol novolak resin (PN-80:Nippon Kayaku Co., Ltd. make --) It blended at a weight rate which it is shown in 2-ethyl-4-methylimidazole (2E4MZ) as hydroxyl equivalent 105 g/eq, 86 degrees C of softening temperatures, and a hardening accelerator, and shows a methyl ethyl ketone (MEK) and methyl cellosolve (MCS) in the column of (combination) of a table 5 as a diluent, and the varnish was prepared. Next actuation was performed like the example 6. A measurement result is shown in a table 5.

[0057]

table 5 [] example 6 Example 6 of a comparison (combination)

E2 100 R-232 100 PN-80 36 22 2E4MZ 0.3 0.3 MEK 82 73 MCS 9 8 (hardened material nature)

Glass transition temperature (degree C) 140 125 Copper foil peel strength (kN/m) 2.8 1.9 Water absorption (%) 0.6 0.5

Dielectric constant 4.6 4.8 [0058] From a table 5, compared with the bisphenol A mold epoxy resin generally used conventionally, the hardened material of this invention is excellent in thermal resistance, adhesion, and a water resisting property, and has a low dielectric.

[0059]

[Effect of the Invention] The epoxy resin constituent containing the epoxy resin of this invention has the thermal resistance which was excellent in the hardened material, adhesion, moisture resistance, and a low dielectric. Therefore, it is very useful when using it for various composite material including the electrical and electric equipment, the insulating material for electronic parts and laminates (printed wired board etc.), or CFRP, adhesives, a coating, etc.

[Translation done.]